

Application No.: 10/629,815

REMARKS

This amendment is filed in response to the Office Action dated November 15, 2007. In view of these amendments and remarks, this application should be allowed and the case passed to issue. No new matter is introduced by this amendment. The amendment to claim 1 is supported by originally filed claim 2. Claim 9 is amended to correct an informality.

Claims 1 and 3-14 are pending in this application. Claim 13 is withdrawn from consideration pursuant to an election of species requirement. Claims 1-12 and 14 are rejected. Claims 1 and 9 are amended in this response. Claim 2 has been canceled in this response.

Objections to the Specification

The specification was objected to as being unclear whether the positive electrode active material precursors are hydroxides or sulfates. This objection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The specification clearly teaches on pages 23-25 that the sulfates are mixed with sodium hydroxide and hydroxides are precipitated from the solution.

As regards the differences between the comparative examples and Example 1, as clearly taught on pages 23-25 the positive electrode active material of the present invention is formed by a coprecipitation process. Whereas, as the comparative example positive electrode active material was formed by mixing powdered lithium hydroxide, powdered nickel hydroxide, and powdered manganese oxyhydroxide and subsequently baking the mixture, as taught on page 50 of the specification.

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Claim Rejections Under 35 U.S.C. § 112

Claims 1-12 and 14 were rejected under 35 U.S.C. § 112, first paragraph, as failing to comply with written description requirement because “uniformly dispersed at the atomic level” is not supported by the disclosure as originally filed. This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The first full paragraph on page 24 clearly support “uniformly dispersed at the atomic level.” Literal support of claim limitation is not required under U.S. patent law. It is clear from the first full paragraph on page 24 that Applicants had possession of the claimed invention and adequately describe the invention to one of ordinary skill in this art. As disclosed on page 24, “since manganese is prone to be oxidized . . . it’s dispersion and formation of solid solution at the atomic level is insufficient.” However, Applicants prevent insufficient dispersion and formation of solid solution at the atomic level and “produce a double hydroxide or triple hydroxide by allowing nickel, manganese, and cobalt elements to be present in one layered hydroxide without separation” by bubbling an inert gas such as nitrogen or argon in the aqueous solution or by adding a reducing agent.

Claims 1-12 and 14 were rejected under 35 U.S.C. § 112, first paragraph, because the specification allegedly does not enable the broad scope of the claims.

The Examiner has not met the burden of establishing a prima facie case of lack of enablement. The Examiner maintained that only one compound, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, is enabled by the disclosure. The examiner has provided no evidence or any basis as to why the claims are not enabled. It is not sufficient to merely argue that a claim is broad to allege lack of enablement. Further, the Examiner is mistaken that only one compound is exemplified. The specification teaches several examples of different positive electrode active materials in Table 5

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on page 54. In addition, the specification (page 2) teaches a number of similar compounds that are outside the scope of the present claims in Table 1. Furthermore, the Examiner did not consider all the *In re Wands* factors, as is required, in reaching the determination of lack of enablement.

Contrary to the Examiner's assertions, claims are not unduly broad and there is great deal of direction provided by the inventors on how to make and use the claimed invention. The present specification includes a detailed explanation of how to form the claimed cathode active materials on pages 23-31 of the present specification. There are a number of working examples in the present specification. Furthermore, as explained in the MPEP § 2164.02, one or no working examples, alone, is not sufficient to sustain a lack of enablement rejection. For example, as the Court explained in *Home Diagnostics v. Lifescan, Inc.*, 381 F.3d 1352 (Fed. Cir. 2004), a single disclosed embodiment does not the scope of the claims to the single embodiment. Therefore, it is abundantly clear that the present specification, which teaches several embodiments, is surely enabling.

The Examiner averred that there is a level of unpredictability in the art. Applicants maintain that there is a level of unpredictability in all inventions. If there were no unpredictability then presumably every invention would be obvious. Applicants maintain that the Examiner-acknowledged level of unpredictability is an indicia of the unobviousness of the claimed invention. In light of the detailed specification supporting the claimed invention, the level of unpredictability and the quantity of experimentation to make and use the present invention is not undue.

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Claims 4 and 7 were rejected under 35 U.S.C. § 112, second paragraph, because it is apparently not understood what "a $[\sqrt{3} \times \sqrt{3}] R30^\circ$ when assigned as R3-m" means. This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

The above terminology is commonly used in crystallography and would be understood by one of ordinary skill in this art. R3-m is a common technical term used to represent a crystallite structure. $[\sqrt{3} \times \sqrt{3}] R30^\circ$ is a technical term used to represent an array of atoms to which attention is paid. For example, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ contains the same number of Ni atoms, Mn atoms, and Co atoms. However, there are many variations in the arrangement of these three atoms. The $[\sqrt{3} \times \sqrt{3}] R30^\circ$ array is one such arrangement. Starting with the Ni atoms, in the case of a p(1X1) array, four Ni atoms are on the sites adjacent to each other, as shown in Kittel, *Introduction to Solid State Physics, 7th Ed.*, attached to this response. The smallest rhombus shown in the left of Fig. 2(a) represents this array. Whereas, in the case of a p(2X2) array, four Ni atoms are on the sites corresponding to the vertices of the rhombus shown in the center of Fig. 2(a). Likewise in the case of the $[\sqrt{3} \times \sqrt{3}] R30^\circ$ array, four Ni atoms are on the sites corresponding to the vertices of the rhombus shown in the right-hand side of Fig. 2(a).

Claim Rejections Under 35 U.S.C. §§ 102 and 103

Claims 1-8, 10-12, and 14 were rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over Ohzuku et al. (Chemistry Letters, CL-010390, Vol. 30 (2001), No. 7, pp. 642-43). The Examiner asserted that CL-010390 discloses a positive electrode material comprising $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. This rejection is traversed, and

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reconsideration and withdrawal thereof respectfully requested. The following is a comparison between the present invention, as claimed, and the cited prior art.

An aspect of the present invention, per claim 1, is a positive electrode active material comprising a lithium-containing composite oxide containing at least nickel and manganese elements, said positive electrode active material comprising primary particles of the composite oxide having a twinning portion, the composite oxide further contains cobalt element, and the nickel, manganese, and cobalt elements are uniformly dispersed at the atomic level. The composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure.

The positive electrode active material of the present invention is not anticipated by or obvious in view of Ohzuku et al. because Ohzuku et al. do not disclose or suggest the composite oxide having a twinning portion and the composite oxide further containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1.

As explained in the declaration under 37 C.F.R. § 1.132 by Dr. Yoshizawa, which was filed February 20, 2007, positive electrode active material fabricated according to Chemistry Letters, CL-010390 exhibit a non-uniform elemental distribution. Exhibit A, as indicated by the widely-separated Co-rich and Co-poor areas, clearly shows a widely varying distribution of cobalt in the Chemistry Letters, CL-010390 positive electrode active material. In contrast thereto, Exhibits A and B clearly illustrate that cobalt is uniformly dispersed throughout the positive electrode material according to the present invention. As illustrated in Exhibits A and

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B, the material according to the present invention is clearly distinguishable over the prior art material.

In the micrographs attached to the declaration, red indicates a high concentration of the element being measured, green represents a low concentration, and yellow represents an intermediate concentration, for each of Ni, Mn, Co. Thus, the Co map only shows Co concentration, the Ni map only shows Ni concentration, and the Mn map only shows Mn concentration.

Because CoCO_3 and nickel manganese hydroxide are used as a raw material in CL-010390, segregation of Co is observed in the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. In contrast thereto, in the present invention a triple hydroxide is used as the raw material (*see* page 24, lines 14-15) resulting in a favorable uniform dispersion of Co.

The Examiner asserted that Ohzuku et al. inherently disclose the claimed material. However, the fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. *In re Rijckaert*, 9 F.3d 1531, 1534, 28 USPQ2d 1955, 1957 (Fed. Cir. 1993). "Inherency . . . may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient." *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999)(citations omitted). In view of the data presented in Dr. Yoshizawa's declaration it is clear that CL-010390 does not inherently disclose the positive electrode active material, as required by claim 1.

The factual determination of lack of novelty under 35 U.S.C. § 102 requires the disclosure in a single reference of each element of a claimed invention. *Helifix Ltd. v. Blok-Lok Ltd.*, 208 F.3d 1339, 54 USPQ2d 1299 (Fed. Cir. 2000); *Electro Medical Systems S.A. v. Cooper*

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Life Sciences, Inc., 34 F.3d 1048, 32 USPQ2d 1017 (Fed. Cir. 1994); *Hoover Group, Inc. v. Custom Metalcraft, Inc.*, 66 F.3d 399, 36 USPQ2d 1101 (Fed. Cir. 1995); *Minnesota Mining & Manufacturing Co. v. Johnson & Johnson Orthopaedics, Inc.*, 976 F.2d 1559, 24 USPQ2d 1321 (Fed. Cir. 1992); *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051 (Fed. Cir. 1987). Because Ohzuku et al. do not disclose positive electrode active material comprising primary particles of the composite oxide having a twinning portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1, Ohzuku et al. do not anticipate claim 1.

Obviousness can be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either in the references themselves or in the knowledge generally available to one of ordinary skill in the art. *In re Kotzab*, 217 F.3d 1365, 1370 55 USPQ2d 1313, 1317 (Fed. Cir. 2000); *In re Jones*, 958 F.2d 347, 21 USPQ2d 1941 (Fed. Cir. 1992); *In re Fine*, F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988). Ohzuku et al. do not suggest positive electrode active material comprising primary particles of the composite oxide having a twinning portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1.

The only teaching of the claimed positive electrode active material comprising primary particles of the composite oxide having a twinning portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the

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composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, is found in Applicants' disclosure. However, the teaching or suggestion to make a claimed combination and the reasonable expectation of success must not be based on applicant's disclosure. *In re Vaeck*, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991).

Claims 1-8, 10-12, and 14 were rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative as obvious over Thackeray et al. (US 2006/0099508). The Examiner asserted that Thackeray et al. disclose $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and the claimed features would have been inherent.

Claim 9 was rejected under 35 U.S.C. § 103(a) as being unpatentable over Thackeray et al. in view of Miyasaka (US 6,416,902). The Examiner alleged that Thackeray et al. do not disclose the claimed primary and secondary particles. The Examiner averred that Miyasaka discloses the primary and secondary particles and that it would have been obvious to make two different particle size distributions to enhance packing because the smaller particles would occupy the voids between the larger particles. The Examiner further pointed out that Miyasaka teaches that secondary particles consist of aggregated primary particles.

These rejections are traversed, and reconsideration and withdrawal thereof respectfully requested.

Initially, it is noted that the Examiner has not established that Thackeray et al. is prior art. Thackeray et al. has a US filing date of November 10, 2005, which is well after the July 30, 2003 filing date of the present application. The Examiner has the burden of proving that the earlier filed priority applications of Thackeray et al. disclose the claimed invention, and the Examiner has not done so. Whether or not Thackeray et al. is prior art, however, the Yoshizawa declaration proves that the claimed "uniformly dispersed" is not inherent and there is no teaching or suggestion in Thackeray et al. of the claimed positive electrode active material comprising

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primary particles of the composite oxide having a twining portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1.

Miyasaka does not cure the deficiencies of Thackeray et al., as Miyasaka does not suggest positive electrode active material comprising primary particles of the composite oxide having a twining portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1.

Claim 9 was rejected under 35 U.S.C. § 103(a) as obvious over Ohzuku et al. (Chemistry Letters, CL-010390, Vol. 30 (2001), No. 7, pp. 642-43) in view of Miyasaka (U.S. Pat. No. 6,416,902). This rejection is traversed, and reconsideration and withdrawal thereof respectfully requested.

Claim 9 depends from claim 1 and is allowable for at least the same reasons as claim 1. The combination of Ohzuku et al. and Miyasaka does not suggest the claimed positive electrode active material because Miyasaka does not cure the deficiencies of Ohzuku et al. Miyasaka does not suggest positive electrode active material comprising primary particles of the composite oxide having a twining portion, containing cobalt element, and the nickel, manganese, and cobalt elements are **uniformly dispersed** at the atomic level, and the composite oxide has a layered crystal structure and the arrangement of oxygen atoms is a cubic close-packed structure, as required by claim 1.

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The dependent claims are allowable for at least the same reasons as independent claim 1, and further distinguish the claimed positive electrode active material.

In view of the above amendments and remarks, Applicants submit that this application should be allowed and passed to issue. If there are any questions regarding this Amendment or the application in general, a telephone call to the undersigned would be appreciated to expedite the prosecution of the application.

To the extent necessary, a petition for an extension of time under 37 C.F.R. § 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

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CHARLES KITTEL

Introduction

to

*Solid State**Physics*

SEVENTH EDITION

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Preface

This book is the seventh edition of an elementary text on solid state physics for senior and beginning graduate students of physical science and engineering. The book is an update of the sixth edition of 1986 and includes additions, improvements, and corrections made in that edition in 13 successive printings which it was time to pull together—and a number of new topics besides. Significant advances in the field have been added or discussed more fully: thus temperature superconductors are treated, and results of scanning tunneling microscopy are displayed; the treatment of fiber optics is expanded. There are discussions, among other topics, of nanostructures, superlattices, Bloch-Weisskopf levels, Zener tunneling, light-emitting diodes, and new magnetic materials. The additions have been made within a boundary condition intended to keep the text within one volume and at a reasonable price.

The theoretical level of the text itself has not been changed. There is a discussion of useful materials. The treatment of elastic constants and electron waves which was dropped after the fourth edition has now been returned because, as many have pointed out, the matter is useful and not easily accessible elsewhere. The treatment of superconductors is much more extensive than usual in a text at this level: either you do it or you don't.

Solid state physics is concerned with the properties, often astonishing, of great utility, that result from the distribution of electrons in materials: semiconductors, and insulators. The book also tells how the excitations (imperfections) of real solids can be understood with simple models whose predictions are now firmly established. The subject matter supports a profitable interplay of experiment, application, and theory. The book, in English and many translations, has helped give several generations of students a picture of the process. Students also find the field attractive because of the frequent opportunity of working in small groups.

Instructors will use the book as the foundation of a course in their way, yet there are two general patterns to the introduction, selection and of the basic material. If students have a significant preparation in elementary quantum mechanics, they will like to begin with the quantum theory of

About the Author

Charles Kittel taught solid state physics at Berkeley from 1961 to 1978; earlier he was a member of the solid state group at the Bell Laboratories. His undergraduate work was at M.I.T. and at Cambridge University, followed by graduate work at the University of Wisconsin. He is a member of the National Academy of Science and of the American Academy of Arts and Sciences.

His research in solids began with studies of ferromagnetic, antiferromagnetic, and paramagnetic resonance, along with work on magnetic domains, spin waves, and domain boundaries in ferromagnets and ferroelectrics. His work on the single domain structure of fine particles has had broad application in magnetic recording, geomagnetism, and biomagnetism. Along with collaborators at Berkeley he did the first work on cyclotron resonance in semiconductors, which led to the understanding of the band structure of silicon, germanium, and indium antimonide, together with the theory of their impurity states. He also worked on the interpretation of magnetoplasma resonance in semiconductors and of Alfvén resonance in electron-hole drops in germanium.

The first edition of *ISSP* integrated the elementary aspects of solid state physics for study by seniors and beginning graduate students. Now in its seventh edition, *ISSP* plays the same part for the current generation of students.

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3. F center. (a) Treat an F center as a free electron of mass m moving in the field of a point charge e in a medium of dielectric constant $\epsilon = n^2$; what is the $1s-2p$ energy difference of F centers in NaCl? (b) Compare from Table 3 the F center excitation energy in NaCl with the $3s-3p$ energy difference of the free sodium atom.

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CHAPTER 19: SURFACE AND INTERFACE PHYSICS

Reconstruction and Relaxation

The surface of a crystalline solid in vacuum is generally defined as the approximately three, outermost atomic layers of the solid that differ significantly from the bulk. The surface may be entirely clean or it may have atoms deposited on it or incorporated in it. The bulk of the crystal is called the substrate.

If the surface is clean the top layer may be either reconstructed or, sometimes, unreconstructed. In unreconstructed surfaces the atomic arrangement in registry with that of the bulk except for an interlayer spacing change (or multilayer relaxation) at the top surface.

The shrinking of the interlayer distance between the first and second of atoms with respect to subsequent layers in the bulk is a rather dominant phenomenon. The surface may be thought of as an intermediate between diatomic molecules and the bulk structure. Because the interatomic distances in diatomic molecules are much smaller than in the bulk, there is a rational surface relaxation. This may be contrasted with reconstruction where relaxation of atoms yields new surface primitive cells. In reconstruction the atoms maintain their structure in the surface plane as it was according to the primitive cell of the bulk; only their distance from the bulk changes.

Experimental values of the top-layer relaxation for metals are given in Table 1. Note the frequency of occurrence of contractions in the interlayer spacing at the surface.

Sometimes in metals, but most often in nonmetals, the atoms in the surface layer form superstructures in which the atoms in the layer are out of registry with the atoms in corresponding layers in the substrate. Surface reconstruction can be a consequence of a rearrangement of broken covalent or ionic bonds at the surface. Under such conditions the atoms at the surface bunch into rows with alternately larger and smaller spacings than in the bulk. That is, some crystals held together by valence bonds, creation of a surface would leave unsaturated bonds dangling into space (Fig. 1). The energy may then be lowered if neighboring atoms approach each other and form bonds with the otherwise unused valence electrons. Atomic displacements can be as large as 0.5 \AA .

Reconstruction does not necessarily require formation of a superstructure. For example, on GaAs (110) surfaces a Ga-As bond rotation occurs that leaves the point group intact. The driving force is electron transfer from Ga to As which fills the dangling bonds on As and depletes them on Ga.

Surfaces of planes normally of high indices may be built up of low index

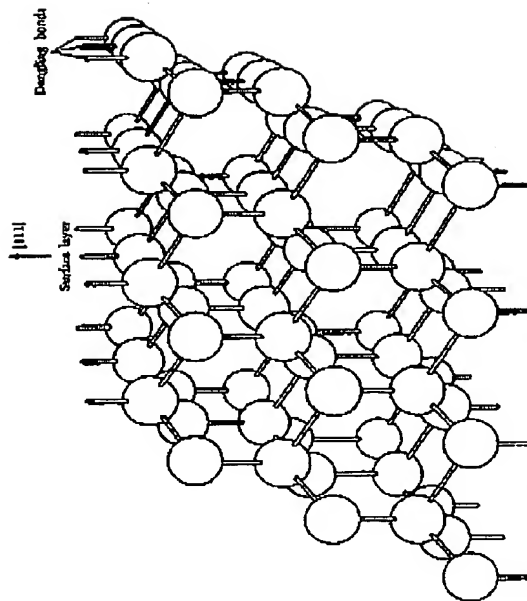


Figure 1 Dangling bonds from the (111) surface of a covalently bonded diamond cubic structure. (After M. Prutton, *Surface physics*, Clarendon, 1975.)

ture; the fifth net is the general oblique net with no special symmetry π between the mesh basis vectors a_1, a_2 . Thus the five distinct nets are oblique, square, hexagonal, rectangular, and centered rectangular.

The substrate net parallel to the surface is used as the reference net f description of the surface. For example, if the surface of a cubic sub crystal is the (111) surface, the substrate net is hexagonal (Fig. 1.9b), an surface net is referred to these axes.

The vectors e_1, e_2 that define the mesh of the surface structure in expressed in terms of the reference net a_1, a_2 by a matrix operation P :

$$\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = P \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

Provided that the included angles of the two meshes are equal, the f hand notation due to E. A. Wood may be used. In this notation, which is u used, the relation of the mesh e_1, e_2 to the reference mesh a_1, a_2 is expressed

$$\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \begin{pmatrix} \Delta_1 & \Delta_2 \\ \alpha_1 & \alpha_2 \end{pmatrix} R \alpha$$

in terms of the lengths of the mesh basis vectors and the angle α of rotation R of the two meshes. If $\alpha = 0$, the angle is omitted. Examples of Wood notation are given in Fig. 2.

The reciprocal net vectors of the surface mesh may be written as c_j defined by

$$c_1 \cdot e_1 = c_2 \cdot e_2 = 0; \quad c_1 \cdot e_1^* = c_2 \cdot e_2^* = 2\pi \text{ (or } 1 \text{)}.$$

Here the 2π (or 1) indicates that two conventions are in use. The definition used in Fig. 3 may be compared with the definitions (2.10) and (2.11) for reciprocal lattice vectors of a triperiodic lattice.

The reciprocal net points of a diperiodic net may be thought of—when are in three dimensions—as rods. The rods are infinite in extent and normal to the surface plane, where they pass through the reciprocal net points. It is helpful to think of the rods as generated by a triperiodic lattice which is extended without limit along one of its axes. Then the reciprocal lattice pc along this axis are moved closer together and in the limit form a rod.

The usefulness of the rod concept comes out with the Ewald sphere construction explained in Fig. 2.8. Diffraction occurs everywhere the Ewald sphere intercepts a reciprocal net rod. Each diffracted beam is labelled with indices hkl of the reciprocal net vector

$$g = h c_1^* + k c_2^*$$

forming the beam.

Low energy electron diffraction (LEED) is illustrated by Fig. 4. The of

Table 1 Relaxation of topmost interlayer spacing at unreconstructed clean metal surfaces

Each entry consists of:

Chemical symbol (interlayer spacing change from bulk value).
(After F. Jona and P. M. Marcus, in "The Structure of Surfaces II," eds. J. F. van der Veen and M. A. Van Hove, Springer-Verlag (Heidelberg, 1988), p. 80)

hcp(0001)	Re (-5%), Sc (-9%), Ti (-5%), Zr (-1%)
fcc(111)	Al (+1%), Ag (0%), Cu (-0.7%), Pt (+1%), Rh (0%)
bcc(110)	Fe (+0.5%), Na (0%), V (-0.3%), W (0%)
fcc(100)	Al (0%), Cu (-1%), Rh (0%)
bcc(100)	Fe (-5%), Mo (-9.5%), Ni (-11%), V (-7%), W (-8%)
fcc(110)	Al (-8.5%), Ag (-8%), Co (-6.5%), Ni (-6.5%), Pb (-10%),
	Rb (-3%)
hcp(10-10)	Re (-17%)
bcc(211)	Fe (-10%), W (-13%)
fcc(311)	Al (-13%), Ni (-15%), Cu (-5%)
bcc(310)	Fe (-15%)
fcc(210)	Al (-15.5%)
bcc(111)	Fe (-17%)
bcc(210)	Fe (-22%)

planes separated by steps one (or two) atoms in height. Such terrace-step arrangements are important in evaporation and desorption because the attachment energy of atoms is often low at the steps and at kinks in the steps. The chemical activity of such sites may be high. The presence of periodic arrays of steps may be detected by double and triple beams of diffraction in LEED (see below) experiments.

SURFACE CRYSTALLOGRAPHY

The surface structure is in general diperiodic. This does not necessarily mean that all its atoms lie in a plane, but rather that the structure is periodic only in two dimensions. The surface structure can be the structure of foreign material deposited on the substrate or it can be the selvege of the pure substrate.

In Chapter 1 we used the term Bravais lattice for the array of equivalent points in two or in three dimensions, that is, for diperiodic or triperiodic structures. In the physics of surfaces it is common to speak of a two-dimensional lattice. Further, the area unit may be called a mesh.

We showed in Fig. 1.9 four of the five nets possible for a diperiodic struc-

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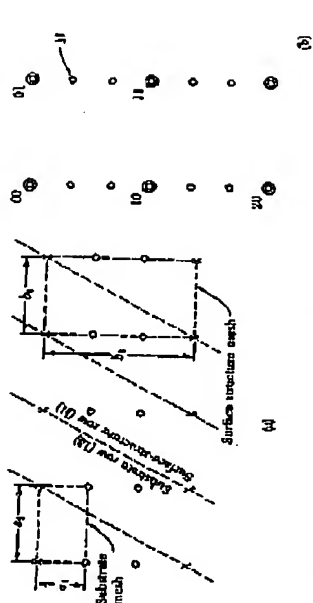


Figure 3 (a) surface structure, (b) reciprocal space diagram (AFx Wood.)

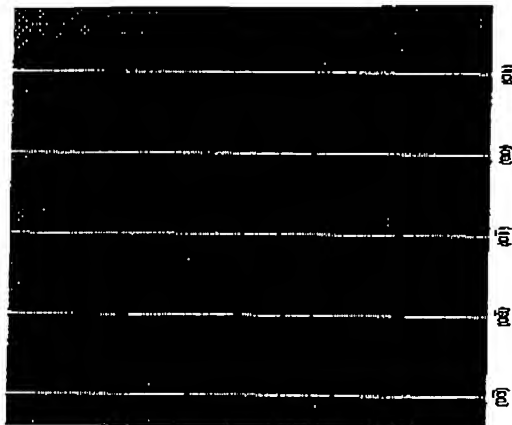


Figure 4 Ewald sphere construction for diffraction of incident wave k by a square net, when parallel to one axis of the mesh. The beam scattered because the plane of the paper are k_1 , k_2 . Diffracted beams out of the plane of the paper will also occur, such as (12) and (13) . These lie on the rods of the reciprocal net.

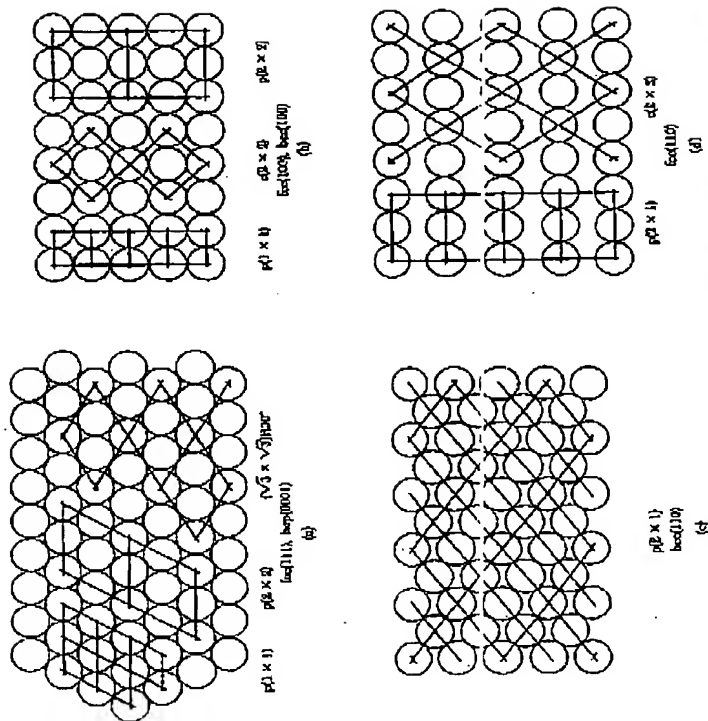


Figure 2 Surface nets of adsorbed atoms. The circles represent atoms in the top layer of the substrate. In (a) the designation $p(2 \times 1)$ means the (11) face of the structure. This face determines a reference net. The lines represent ordered overlayers, with additional at the intersections of two lines. The intersection points represent dipole moments (lattices in two dimensions). The designation $p(2 \times 1)$ in (a) is a primitive mesh unit for which the basis is identical with the basis of the reference net. In (b) the $p(2 \times 2)$ mesh unit is a centered mesh with basis vectors twice as long as those of the reference net. Atomic adsorption on mesh tubes place most often into these surface sites (yellow stars) that maximize the number of nearest-neighbor atoms on the substrate. (After Van Hove.)

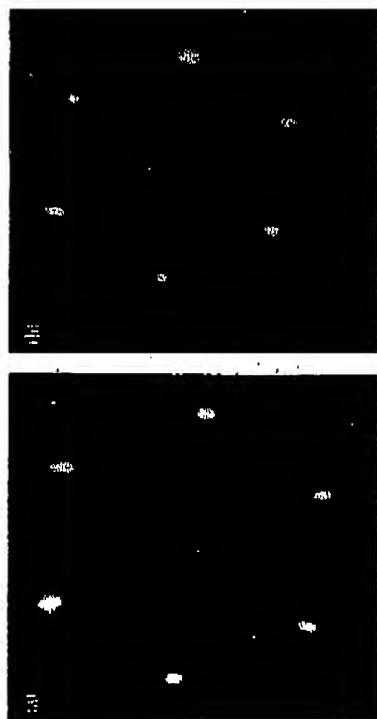


Figure 5. LEED patterns from a Pt(111) crystal surface for incident electron energies of 51 and 52 eV. The diffraction angle is greater at the lower energy. (After G. A. Somorjai, *Chemistry in two dimensions: surfaces*.)

iron energy is typically in the range 10–1000 eV. This is the arrangement with which Davisson and Germer in 1927 discovered the wave nature of the electron. An experimental pattern is shown in Fig. 5.

Reflection High-Energy Electron Diffraction. In the RHEED method a beam of high-energy electrons is directed upon a crystal surface at grazing incidence. By adjustment of the angle of incidence one can arrange the normal component of the incoming wavevector to be very small, which will minimize the penetration of the electron beam and enhance the role of the crystal surface.

The radius k of the Ewald sphere for 100 keV electrons will be $\approx 10^3 \text{ \AA}^{-1}$, which is much longer than the shortest reciprocal lattice vector $2\pi/a \approx 1 \text{ \AA}^{-1}$. It follows that the Ewald sphere will be nearly a flat surface in the central scattering region. The intercept of the rods of the reciprocal net with the nearly flat sphere will be nearly a line when the beam is directed at grazing incidence. The experimental arrangement is shown in Fig. 6.

SURFACE ELECTRONIC STRUCTURE

Work Function

The work function ϕ of the uniform surface of a metal is defined as the difference in potential energy of an electron between the vacuum level and the Fermi level. The vacuum level is the energy of an electron at rest at a point sufficiently far outside the surface so that the electrostatic image force on the

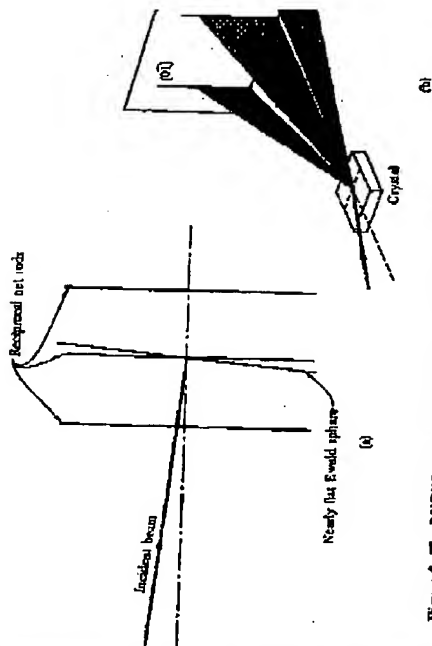


Figure 6. The RHEED method. In (a) the high energy incident electron beam at a grazing angle to the crystal surface is shown. In (b) the Ewald sphere is large radius, so large that the surface nearly flat in relation to the separation between adjacent rods of the reciprocal net. The diffraction pattern is shown in (b). (After Fruton.)

electron may be neglected—more than 100 Å from the surface. The Fermi level is the electrochemical potential of the electrons in the metal.

Typical values of electron work functions are given in Table 2. The orientation of the exposed crystal face affects the value of the work function because the strength of the electric double layer at the surface depends on the concentration of surface positive ion cores. The double layer exists because the surface ions are in an asymmetrical environment, with vacuum (or an adsorbed foreign atom layer) on one side and the substrate on the other side.

The work function is equal to the threshold energy for photoelectric emission at absolute zero. If $h\nu$ is the energy of an incident photon, then the Einstein equation is $h\nu = \phi + T$, where T is the kinetic energy of the emitted electron and ϕ is the work function.

Thermionic Emission

The rate of emission of thermionic electrons depends exponentially on the work function. The derivation follows.

We first find the electron concentration in vacuum in equilibrium with electrons in a metal at temperature T ($=k_B T$) and chemical potential μ . We treat the electrons in the vacuum as an ideal gas, so that their chemical potential is

$$\mu = \mu_{\text{vac}} + k_B T \ln(n/n_0) \quad (5)$$

by T , Chapter 8. Here